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INFO MISSILE TECHNOLOGY CONTROL REGIME COLLECTIVE PRIORITY

C O N F I D E N T I A L STATE 104822

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E.O. 12958: DECL: 10/01/2033
TAGS: MTCRE ETTC KSCA MNUC PARM TSPA FR UK AS

SUBJECT: MISSILE TECHNOLOGY CONTROL REGIME (MTCR): THE PERCHLORATE FAMILY OF CHEMICALS

Classified By: ISN/MTR Director Pam Durham.
Reasons: 1.4 (B), (D), (H).

¶1. (U) This is an action request. Please see paragraph 2.

¶2. (C) ACTION REQUEST: Department requests Embassy Paris provide the interagency cleared paper "The Perchlorate Family of Chemicals" in paragraph 3 below to the French Missile Technology Control Regime (MTCR) Point of Contact (POC) for distribution to all Partners. Department also requests Embassy London provide paper to the MTCR Information Exchange (IE) Co-Chair (John Andrews), and Embassy Canberra provide paper to the Australian MTCR Plenary Chair for 2008/2009 and/or appropriate staff. Info addressees also may provide to host government officials as appropriate. In delivering paper, posts should indicate that the U.S. is sharing this paper as part of our preparation for the Information Exchange that will be held in conjunction with the MTCR Plenary in Canberra (November 3-7). NOTE: Additional IE papers will be provided via septels. END NOTE.

¶3. (C) BEGIN TEXT OF PAPER:

(CONFIDENTIAL REL MTCR)

The Perchlorate Family of Chemicals

Perchlorate is the chemical name used for the salts of perchloric acid. All perchlorates are strong oxidizing agents, and as such, they have found application in energetic formulations to include propellants, explosives, and pyrotechnics. Numerous perchlorate salts exist. However, this paper will only deal with ammonium perchlorate (NH_4ClO_4, AP), potassium perchlorate ($KClO_4$, KP, or PP) and sodium perchlorate ($NaClO_4$, NaP, or SP) because of either their energetic properties or their potential use in creating more energetic perchlorates. AP is the most important perchlorate in terms of solid propellants for ballistic missiles and is controlled specifically by the Missile Technology Control Regime (MTCR). Neither KP nor NaP is controlled specifically by the MTCR. KP has limited value in solid propellants for ballistic missiles, although it may be used in a mixture for igniters. There is no known use of NaP directly in solid propellants for ballistic missiles. However, both NaP and KP can be converted to AP.

This paper will discuss the preparation of perchlorates, the use of perchlorates in energetic formulations with emphasis on solid propellants for ballistic missiles, and the current MTCR controls on perchlorates.

Preparation of Perchlorates

Almost all commercial perchlorate preparation-including that of AP and KP-involves the oxidation of sodium chloride to sodium perchlorate. Sodium perchlorate is most often

converted to the other more widely used perchlorate salts including AP and KP, but can also be used itself in some applications.

Complete preparation of perchlorates can be costly in terms of resource consumption and technical expertise. Both processes, oxidation to sodium perchlorate and conversion of sodium perchlorate to other perchlorate salts, require some degree of technical know-how and equipment. The oxidation process is a larger technical challenge and requires more specialized equipment. On the other hand, conversion of sodium perchlorate to AP or KP is much simpler, and the purchase of sodium perchlorate may be more attractive to programs of concern since it avoids the expense and difficulties of the sodium perchlorate oxidation process. Therefore, the lack of MTCR control on sodium perchlorate allows for the potential for a country/entity to make AP with less investment in equipment, facilities, and process engineering.

Oxidization of Sodium Chlorate and Sodium Perchlorate

The oxidation of sodium chloride to sodium perchlorate is conducted in two stages. Sodium chloride (NaCl) is first oxidized to sodium chlorate ($NaClO_3$) and then to sodium perchlorate ($NaClO_4$). Both oxidation stages are electrolytic (electrochemical) processes conducted in aqueous solution. Water is the source of oxygen incorporated into the chloride to make the chlorate and perchlorate species. Sodium chloride is the best starting material for the synthesis of chlorates and perchlorates by this process because all of the sodium salts (chloride, chlorate, and perchlorate) are readily soluble in water.

The oxidation of sodium chloride to sodium chlorate and sodium perchlorate normally requires two steps and requires specialized equipment (electrolytic cells and anodes) and substantial technical knowledge to engineer the process and to make and maintain the equipment. The oxidation steps also require significant electrical power input, and the cost of the electrical power must be reasonably inexpensive to make low-cost perchlorate. The second stage of the oxidation process requires substantially more electric power because it becomes more difficult to add the fourth oxygen atom to the molecule in the conversion of chlorate to perchlorate.

At the completion of the second oxidation stage, sodium perchlorate, typically in the form of its monohydrate ($NaClO_4$ with one H_2O) can be obtained from the aqueous solution by concentration, precipitation, and filtration. However, since sodium perchlorate has only limited uses, the aqueous solution of sodium perchlorate is more often used in the preparation of other perchlorates such as AP and KP.

Conversion of Sodium Perchlorate to AP and KP

Both AP and KP are less water soluble than NaP. Therefore, they can readily be precipitated from an aqueous solution of NaP by addition of the appropriate ammonium or potassium salt. For example, to make AP, ammonium chloride can be added to precipitate AP and leave the very soluble sodium chloride in solution. Conversely, to make KP, potassium chloride is added to precipitate KP and leave sodium chloride in solution. Both AP and KP can be isolated in good yield by concentration, precipitation, and filtration. The isolated perchlorate (either AP or KP) is typically recrystallized from water to obtain the desired purity and particle size before further use.

The process equipment used to convert sodium perchlorate to AP or KP is not specialized and involves relatively low technology. It is an ordinary assemblage of steel, tanks, pumps, heat exchanger, and piping.

Other Conversion Processes for KP to AP

Processes to convert KP to AP have been reported in the chemical literature and several patents exist. These processes will not be discussed in detail, however, as they generally involve non-aqueous solvents and/or ion exchange resins. The use of these types of organic materials with perchlorates poses increased safety risks (fire and explosion) compared to the aqueous process used in the conversion of NaP to AP. Furthermore, we are not aware of the large-scale, commercial demonstration of any of the processes for converting KP to AP. However, the existence of these potential processes for conversion of KP to AP must be acknowledged. These processes could be used by a country/entity that needs AP, but lacks the ability to make/obtain NaP and has access to KP.

Uses of AP, KP, and NaP

AP is the most widely used oxidizer in solid propellant formulations. AP can also be used in explosive and pyrotechnic formulations. Typical composite propellants contain 60 to 70% AP. Solid rocket motors used in the various stages of ballistic missiles are loaded with thousands of kilograms of propellant. Therefore, large quantities of low-cost, high-quality AP are required to make a substantial number of ballistic missiles of any type.

KP can be used as an oxidizer in solid propellant formulations, but it is inferior to AP in terms of performance. The theoretical specific impulse values of KP-based formulations are approximately 15% lower than corresponding AP-based formulations. The low performance compared to AP is the principle reason KP is not widely used in ballistic missiles. However, in the past KP has been used in some solid rocket motors for ballistic missiles and battlefield rockets.

KP cannot be used as a direct substitute for AP, and any substitution would require a complete redesign of the solid propellant rocket motor. In addition to lower specific impulse performance, formulations containing KP have higher density values (KP is denser than AP), different burning characteristics (burning rate, pressure exponent, temperature sensitivity), and signature (KCl is a combustion species) than formulations containing AP, all of which are key factors for solid rocket motor design. This replacement of oxidizers would most likely require significant design changes and a motor requalification effort.

KP is widely used as the oxidizer in explosive and pyrotechnic formulations. The Merck Index lists other uses for KP in photography, analytical chemistry, and in at least some medical treatments. Most of the explosive formulations with KP are used for commercial purposes since military explosives typically contain high energy explosives such as PETN, HMX, and RDX. Furthermore, the use of KP and other perchlorates in commercial explosives has diminished recently due to environmental concerns over groundwater contamination by perchlorates. The pyrotechnic formulations with KP include automotive airbag inflation units, fireworks, flares, and initiation/ignition materials.

Sodium perchlorate has only limited uses, and is used primarily as a precursor to the other perchlorate salts-especially AP and KP. The use of sodium perchlorate in energetic formulations is hampered significantly by its tendency to pick up moisture. The fact that its most stable crystalline form is a monohydrate also makes it less attractive in energetic formations. Like KP, sodium perchlorate has been used in explosive and pyrotechnic formulations and to treat hyperthyroidism, although such uses do not appear to be widespread.

Current MTCR Control of Perchlorates

The MTCR Technical Annex contains several items dealing with perchlorates in general as well as specific perchlorates.

MTCR Technical Annex item 4.C.3 controls any perchlorate when

it is mixed with powdered metals or other high energy fuel components. Binary mixtures of a perchlorate with a powdered metal or a high energy fuel component would be expected to be extremely dangerous to handle. Therefore, this section of the MTCR Technical Annex deals with complete formulations or sub-mixes where sufficient other ingredients are present to make the combination safe to handle. Complete formulations are often shipped in ignition devices or some other smaller component of a ballistic missile.

Specific perchlorates are mentioned in MTCR items 4.C.2.b.16 (hydrazinium perchlorate), 4.C.2.b.17 (hydrazinium diperchlorate), and 4.C.4.b.1 (ammonium perchlorate). Of these specifically controlled perchlorates, AP is the most important to solid propellant formulations for ballistic missiles.

Sodium perchlorate and potassium perchlorate are not specifically controlled by the MTCR. Individually, neither sodium perchlorate nor potassium perchlorate can be directly used in the manufacture of solid propellant formulations used in ballistic missiles. However, both sodium perchlorate and potassium perchlorate are of concern -- SP to a greater degree -- and both can be used as precursors for AP production. Therefore, a country/entity that desires AP for use in ballistic missiles but lacks the ability to oxidize chlorides to perchlorates could obtain sodium perchlorate or potassium perchlorate and convert it to AP.

END TEXT OF PAPER.

¶4. (U) Please slug any reporting on this or other MTCR issues for ISN/MTR. A word version of this document will be posted at www.state.sgov.gov/demarche.
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